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Ion velocities of laser desorbed ions passing through quadrupole electric fields

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ABSTRACT

This paper is a study of the effects of quadrupole electric fields on the velocities of ions generated by laser desorption ionization (LDI). We used a charge detector to measure ion flight time in the absence of electric and magnetic fields to obtain the initial velocity distribution of ions generated in the LDI process. It was found that the measured ion velocity of fullerene and matrix ions was proportional to the energy of the laser pulse. Then we measured velocity distributions of fullerene ions in rf-only quadrupoles. It was observed that the electric field in the fringing field region was proportional to pseudo-potential well depth (D_z) and that ions gained velocity in the fringing field region and speeded up as the D_z was increased due to transfer of rotational energy into translational energy in the high-order field region. Initial velocity of ions passing through different stages of quadruple was increased at every stage. In addition, the mass spectrometric analysis showed when the rf amplitude was low, the quadrupole field allowed stable motion of low mass ions; when the rf amplitude was increased, effective potential well depth was reduced. This is evident that the gradient of ion velocity drops as the difference in D_z increases for C_{60} and high mass C_n cluster ions.

1. Introduction

Measurement of ion velocity has drawn considerable attention in physics and chemistry [1,2]. This measurement can help to understand the mechanism of matrix-assisted laser desorption ionization (MADLI) [3,4] and it has been proposed that initial ion velocity is crucial to explain the mechanism [5,6]. To obtain information about initial ion velocity distributions, time-of-flight (TOF) mass spectrometry (MS) instruments are conventionally used [5–10]. Spengler and Kirsch developed a two-stage acceleration linear MALDI-TOF MS to create homogeneous electrostatic fields during ion formation in which ions were delayed and then extracted for initial velocity measurements [11]. However, the time scale of MALDI ion formation was typically about 20 μs [1], so the time for plume development in the ion formation region was too short (∼ns) for initial ion velocity measurement by MALDI TOF-MS. Therefore, Zenobi et al. proposed a matrix assisted laser desorption/ionization Fourier transform ion cyclotron resonance (MALDI FT-ICR) mass spectrometer to develop plume so that the ions could fly into the ICR trap and the initial ion velocity could be measured [12,13]. However, they observed that ion flight time was perturbed by the magnetic field in the radial direction and thus initial ion velocity measurements might have been affected.

Quadrupoles are generally used in mass spectrometric instruments to transmit ions at different vacuum stages [14] and rf-only quadrupoles are considered velocity selectors [15] as well as mass filters [16]. Rf-only quadrupoles are developed to improve transmission of ions by incorporating collision cooling in different vacuum chambers [17,18]. Besides, controlling ion kinetic energy is critical when transferring ions to mass analyzers, for example between two quadrupole ion traps [19–21] and a quadrupole to a TOF [22,23]. Majidi et al. [23] experimentally studied the transmission properties of rf-only quadrupoles when atmospheric pressure ionization sources coupled with TOF-MS and examined the effect of dc bias potential of quadrupole and skimmer voltage on axial velocity of different m/z ions. Transmitting ions from one chamber to another chamber would result in gain or loss of ion energy due to diminution of electric fields in the fringing field region at the entrance and exit of quadrupoles [24–26]. Brinkman [26], Leck [27,28] and Dawson [29] reported that when ions entered and exited rf-only quadrupoles, they gained or lost energy. In the fringing field region, ions can gain more energy by coupling radial and

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axial fields [30]. This characteristic of fringing fields is applied in mass selective axial ejection of ions [16,30–32]. Londry and Hager [30] developed analytical theory and computer modeling to understand the characteristics of fringing fields and some researchers conducted phenomenological studies to explore the topic as well [28,31,33]. Those studies of fringing fields were mainly focused on single quadrupole or on an ion trap operating with axial ion ejection. That is to say, prior to axial ion ejection, the radial position of ions was well defined in the quadrupole or ion trap [30]. After ions were ejected out, ions were influenced by the fringing field of quadrupole or ion trap. However, no quantitative measurement has been done on velocity gain in the fringing field region, especially when ions travel through multi-quadrupoles.

The aim of this paper is to study ion velocities with and without the influence of electric fields. First, we introduced a novel method for the measurement of initial velocities of laser desorption ions (LDI) in the absence of electric and magnetic field. We conducted measurement of ion flight time by a charge detector to obtain the initial velocity distribution of ions generated in the laser desorption ionization (LDI) process. These results confirmed that without field interference the velocity distributions of C_{60} ions and of the matrix ions are linearly proportional to the laser pulse energy. Then we used rf-only quadrupoles to do quantitative measurements on the gain of ion velocity and a formula was derived. With quadrupole fields, the electric field strength in the fringing field region is proportional to the pseudo-potential well depth (D_z). It was also observed that the velocity of C_{60} ions was increased with the D_z parameter. At higher D_z value, ions could be focused on the axial direction of the quadrupoles and therefore the radial displacement of ions (ion defocusing) was rarely resulted. In a multi-quadrupoles system, when ions passed through more quadrupoles, ion velocities increased constantly at every stage of quadrupoles. It is noticed when the rf amplitude was low, the quadrupole field allowed stable motion of low mass ions; when the rf amplitude was increased, reduction of effective pseudo-potential well depth occurred [34]. This is due to the gradient of ion velocity drops as the difference in pseudo-potential well depth increases for C_{60} and high mass C_n cluster ions, causing unstable motion of C_{60} ions and stable motion of high mass C_n clusters. Our mass spectrometric analysis also supported the above observations, that is, high mass C_n clusters ions could pass the quadrupoles at high D_z settings and could be trapped by the rectilinear ion trap but C_{60} ions were not stable and could not be trapped by rectilinear ion trap.

2. Experimental

2.1. Sample and reagent preparation

MALDI matrices of sinapic acid (SA) and α-cyano-4-hydroxycinnamic acid (CHCA) were purchased from Fluka and Sigma, respectively. Fullerene (C_{60}, purity >99%, with C_{70} as the major impurity) was purchased from UniRegion Bio-Tech. Toluene, acetone and methanol were purchased from J.T. Baker. The above compounds were used as received. A sample 6 μl of a 1.4 mM solution of fullerene was prepared in toluene and loaded on the sample probe. Matrix solutions with concentrations of 5 mg/mL in 80% acetone/methanol (MeOH) (v/v) for CHCA and 6 mg/mL in 60% MeOH/acetone (v/v) for SA was prepared and placed to air dry on a sample probe.

2.2. Experimental setup for velocity measurement in the absence of electric field

A schematic diagram of the field-free MALDI/LDI initial ion velocity measurement setup is shown in Fig. 1a. Samples were loaded on a stainless steel probe and introduced by a transfer rod into a vacuum chamber which was evacuated to a pressure of 5×10^{-5} Torr. The sample probe was irradiated by a pulsed Nd:YAG laser at the angle of 45° from the surface normal and ions were generated on the detector axis. The charge detector was located at a distance l from the sample probe. The ion flight time (t) was measured by 500 independent laser shots. No ion optical elements were located between the sample probe and the charge detector. The procedure used to measure the initial velocity distribution of ions generated by MALDI/LDI is free of any influence of electrostatic and magnetic field penetration. The flight time of ions was measured by synchronization of a charge detector and a laser Q-switch trigger, and a computer was used to collect data with data acquisition cards NI PCI 6251 and NI PCI 6281 (National Instruments, Austin, TX) as shown in Fig. 1b. The measured flight time of ions was converted to the ion velocity distribution (Fig. 1c).

Table 1
rf voltage (V_{p-p}), q_z values and pseudo-potential well depth D_z applied on quadrupoles Q1, Q2, Q3. And q_z and D_z values of RIT were calibrated with C_{60} positive ions (m/z = 720 Th).

V_{p-p} (rf only)	q_z (Q1, Q2, Q3)	D_z (Q1, Q2, Q3)	q_z (RIT)	D_z (RIT)
100	0.218	2.74	0.218	2.74
150	0.328	6.15	0.328	6.15
200	0.438	10.95	0.438	10.95
250	0.548	17.11	0.548	17.11
300	0.657	24.65	0.657	24.65
350	0.767	33.55	0.767	33.55
400	0.876	43.80	0.876	43.80
450	0.986	55.45	0.986	55.45

2.3. Experimental setup for velocity measurement in the presence of electric field

Fig. 2 shows how ion velocity measurements were carried out by means of a multi-quadrupole rectilinear ion trap (RIT) mass spectrometer in rf-only mode and ions were detected with the charge detector. The system comprises a MALDI ion source, a square quadrupole (Q1), a bent square quadrupole (Q2), a square quadrupole (Q3), a RIT mass analyzer, a charge detector and an electron multiplier. In order to examine how ion velocity changes in a multi-quadrupoles system, the experimental design is simplified to setup 1 (Q1 + Q2), setup 2 (Q1 + Q2 + Q3) and setup 3 (Q1 + Q2 + Q3 + RIT) as shown in Fig. 2a–c respectively. A charge detector was placed behind the skimmer in setup 1 and the lens 2 in setup 2 to measure the ion velocity. With setup 1 and setup 2, the correlation of ion velocity and pseudo-potential well depth can be studied at a fixed laser energy density of 0.68 mJ/cm^2. In the setup 1 (Q1 + Q2), ions were guided through the quadrupoles Q1 and Q2, which were operated at fixed frequencies $\Omega = 2\pi \times 640$ kHz, and $\Omega = 2\pi \times 842$ kHz, respectively. A charge detector was placed after skimmer to measure the ion flight time. The ion flight time was measured at different settings of pseudo-potential well depth introduced in Table 1. In the setup 2 (Q1 + Q2 + Q3), ions were guided through Q1 and Q2, and a quadrupole Q3 was operated at fixed frequency $\Omega = 2\pi \times 635$ kHz. The charge detector was placed behind lens 2. The q_z values of all three quadrupoles Q1, Q2 and Q3 were also kept consistent throughout velocity measurements in both setups. RIT was introduced after Q3 to acquire the mass spectra. In the setup 3 (Q1 + Q2 + Q3 + RIT), the experimental conditions of Q1, Q2 and Q3 were the same as those of the setup 2 and the RIT was operated at a fixed frequency $\Omega = 2\pi \times 360$ KHz. The charge detector was placed behind the end-cap lens (lens 3) of RIT to measure the ion flight time. Because the dimensions of quadrupole ion guides are different, the settings of frequency and voltage are different in order to match the pseudo-potential well